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Fine particulates, with dimensions of 10 microns or less, offer a unique opportunity to study phase transitions between the liquid and solid states as well as a means to obtain material properties for undercooled liquids not obtainable in bulk samples. These advantages are exploited in both metal powder and ceramic powder processing technology. In fact, metal powders find many applications where homogeneous structures are beneficial. Such homogeneous structures being obtained by segregationless solidfication at high undercooling. Representative applications for controlled narrow size distribution metal powders include superalloys, superplastic aluminum alloys, composite materials, magnetic recording

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19. Abstract

media, ferrofluids and conducting plastics. Developments in Rapid Solidification Processing (RSP) have enabled superalloy powders to be used for high temperature and pressure applications. RSP metal and alloy powders are typically produced through atomization from-the-melt processes. While morphology of the powders are excellent (spherical) under the correct processing conditions, size distributions are usually broad and skewed to larger sizes due to non-uniform breakup of the molten metal stream prior to droplet freezing. Mechanical separation (sieving) must be performed to upgrade and narrow the resultant size distribution.

As an alternative to Rapid Solidification Processing, low temperature reduction has been reintroduced as a way to produce uniform metal powders through chemical precipitation. Many metals may be chemically quenched to non-equilibrium states by precipitation at low temperatures. In the current technology, metal powders are produced from solution using polyols and other polar nonaqueous organic solvents as both solvent for the metal salt and reductant to the metal ion. Early application of this technology dates back to 1926 when pyrophoric lead powder was obtained by thermal decomposition of lead glyceroxide produced through reaction of lead acetate in glycerol. Finely divided metallic copper powder has been produced by reacting copper salts in glycerol heated to 423-473K. These reports form the basis for the chemical technique that is employed in the production of metal powders that were utilized here in research on the nucleation/undercooling of liquid metals.

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Undercooling and Nucleation in Rapid Solidification Rate Metal Powders Using Solid in Solid Emulsification

Prepared by

Dr. Donald Rasmussen
Dept. of Chemical Engineering
Clarkson University
Potsdam, NY 13676

Submitted to:

U.S. Army Research Office
Research Triangle Park
North Carolina 27709-2211

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Fine particulates, with dimensions of 10 microns or less, offer a unique opportunity to study phase transitions between the liquid and solid states as well as a means to obtain material properties for undercooled liquids not obtainable in bulk samples. These advantages are exploited in both metal powder and ceramic powder processing technology. In fact, metal powders find many applications where homogeneous structures are beneficial. Such homogeneous structures being obtained by segregationless solidification at high undercooling. Representative applications for controlled narrow size distribution metal powders include superalloys, superplastic aluminum alloys, composite materials, magnetic recording media, ferrofluids and conducting plastics. Developments in Rapid Solidification Processing (RSP) have enabled superalloy powders to be used for high temperature and pressure applications. RSP metal and alloy powders are typically produced through atomization from-the-melt processes. While morphology of the powders are excellent (spherical) under the correct processing conditions, size distributions are usually broad and skewed to larger sizes due to non-uniform breakup of the molten metal stream prior to droplet freezing. Mechanical separation (sieving) must be performed to upgrade and narrow the resultant size distribution.

As an alternative to Rapid Solidification Processing, low temperature reduction has been reintroduced[1,2] as a way to produce uniform metal powders through chemical precipitation. Many metals may be chemically quenched to non-equilibrium states by precipitation at low temperatures. In the current technology, metal powders are produced from solution using polyols and other polar nonaqueous organic solvents as both solvent for the metal salt and reductant to the metal ion. Early application of this technology dates back to 1926 when pyrophoric lead powder was obtained by thermal decomposition of lead glyceroxide produced through reaction of lead acetate in glycerol[3]. Finely divided metallic copper powder has been produced by reacting copper salts in glycerol heated to 423-473K[4]. These reports form the basis for the chemical technique that is employed in the production of metal powders that were utilized here in research on the nucleation/undercooling of liquid metals.

I. METAL POWDER GENERATION

The preparation of uniform, fine metal powders has been driven by the need of a very narrow size distribution metal powder sample - on the order of a micron or less in diameter - for use in nucleation/undercooling research. Commercially available powders, manufactured from atomization techniques, are very broad in size distribution. These commercial samples are also not satisfactory for nucleation rate research because they have experienced high temperature preparation and possible surface oxidation. Using a nonaqueous solution reduction technique, uniform metal powders of cobalt,

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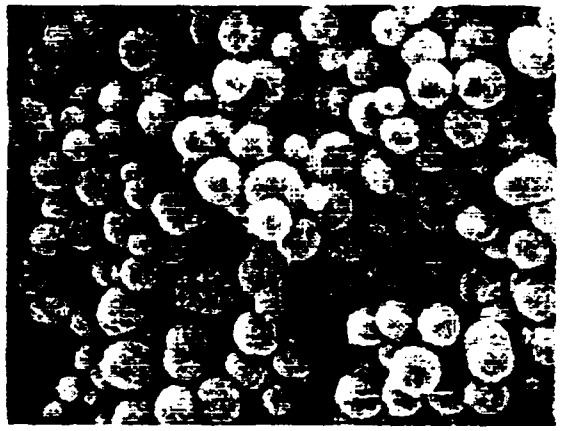
nickel and Co-Ni alloys as well as copper, silver and lead were produced[5]. These powders have narrow size distributions which make them suitable for nucleation/undercooling research.

Metal powders of narrow size distribution have been prepared by both homogeneous and heterogeneous reduction from non-aqueous solutions of cobalt, copper, lead, nickel and silver. The control of the reduction process is achieved by temperature control for the thermal decomposition of the solvent into reductant and/or by the use of laser excitation of the decomposition of the metal ion complexes in solution[6]. Uniform metal particle nucleation with controlled-growth enables powders to be precipitated from solution with well defined size distribution and morphology. Key parameters affecting the powder production by thermal decomposition of the solvent are reaction temperature, reductant/solvent choice, added surfactant chemistry and concentration, stirring-rate, initial metal salt and, when necessary, hydroxide precipitating base concentration. The metal powders produced can be equiaxed or platelet crystals with sharp corners, be crystallographic forms with rounded corners and edges, or be spherical with surface morphologies ranging from crystallographically smooth to fuzzy or rose-petal rough or finally, be unique unexpected shapes. The mean diameter, d, for the powders are normally within the range of from 0.1 to 7 microns. For narrow size distributions, the sample standard deviations are on the order of 0.1 d. Differential thermal analysis indicates melting points in excellent agreement with pure bulk standards, suggesting low impurity contamination. X-ray powder diffraction patterns generally show equilibrium structures are formed though for a microcrystalline cobalt sample prepared from the $Co(OH)_2$ precursor a near amorphous powder pattern is obtained. Magnetic measurements on the cobalt material indicate that the sample is probably fully microcrystalline however[7]. The microcrystalline cobalt transforms on heating to 678 K to a macroscopic but nonequilibrium crystal structure. Further heating to 1200 K transforms the cobalt to its equilibrium form.



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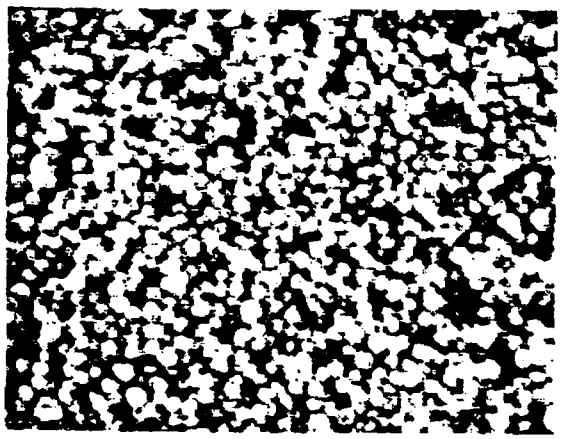

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Figure 1. Top photomicrograph. Cobalt powder from $Co(OH)_2$ precursor. Bottom photomicrograph. Cobalt powder from $CoCl_2$ precursor.

A. COBALT AND NICKEL POWDERS

Cobalt, nickel and Co-Ni alloy powders were prepared by a low-temperature non-aqueous solution technique using polyols such as ethylene glycol as solvent and reductant. The starting materials were cobalt hydroxide, cobalt chloride hexahydrate, cobalt acetate tetrahydrate, nickel hydroxide, nickel chloride hexahydrate and nickel acetate tetrahydrate. These powders were supplied by Aesar and Aldrich and all were reagent grade. Sodium hydroxide, supplied by J.T. Baker, was used to both precipitate the metal hydroxide from non-aqueous solution and to catalyze the reduction reaction. The non-aqueous solvents were ethylene and tetraethylene glycol (reagent grade) supplied by Aldrich. Metal powders were made by reacting the above metal salts with NaOH in the glycol in a 250 ml pyrex 3-necked reaction flask, mechanically stirred with either a glass shaft/teflon blade or a stainless steel shaft/impeller.

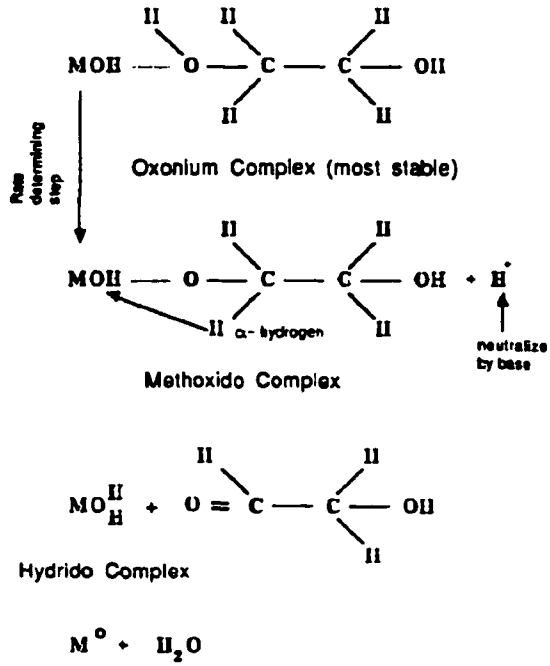


Figure 2. Proposed general mechanism of reduction in polyols.

The reactor was heated with an electric heating mantle by Electothermal Engineering LTD., and a water-cooled condenser provided internal reflux. The flask was either purged with nitrogen gas or was open to the atmosphere through the condenser. The reaction temperature was typically at the boiling point, 470K for ethylene glycol and approximately 587K for the tetraethylene glycol based solutions. Time needed for complete reaction varied from approximately 24-48 hrs for commercial hydroxide starting components to 4-6 hrs for precipitated hydroxide from metal salt/catalyzed reactions with NaOH. The precipitated metal powders were filtered and washed repeatedly in methanol and dried overnight in air. The powder was then ready for DTA and SEM analysis and any further heat treating. Even the very fine, submicron metal powder was not pyrophoric.

Figure 1 contains SEM photomicrographs of cobalt powders precipitated from commercial cobalt hydroxide/ethylene glycol and cobalt chloride hexahydrate/sodium hydroxide/ethylene glycol refluxed solutions, respectively. Both powders are spherical and narrowly-dispersed in relation to size. The surface morphology differs between the samples with the commercial hydroxide source material having a more diffuse appearance than the chloride salt-based product. This suggests differing particle-growth

environments for the two chemistries. The two chemistries may correspond to differing complex stability

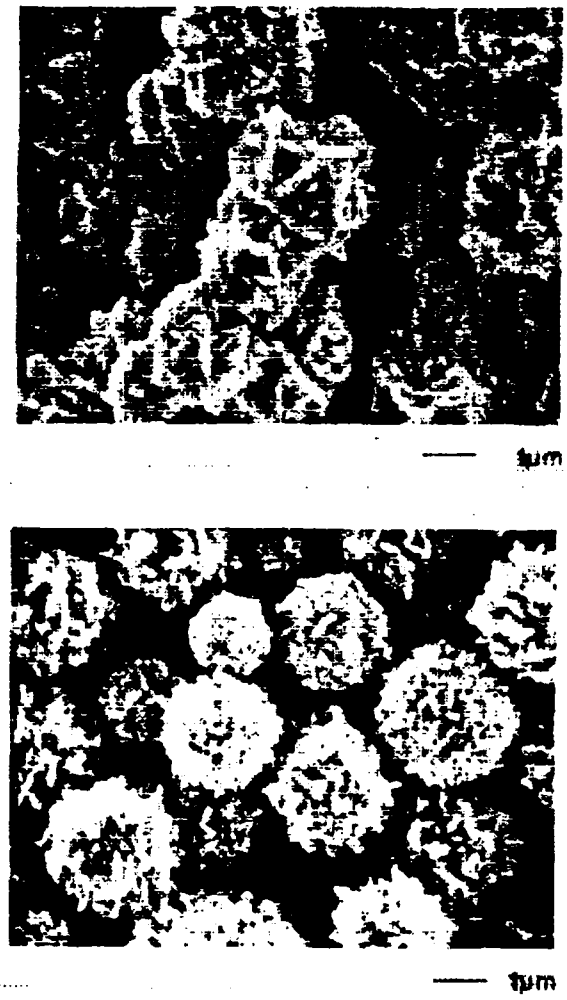


Figure 3. Top photomicrograph. "Aspherical" Cobalt Powder. Baottom photomicrograph. "Roselike" Cobalt powder.

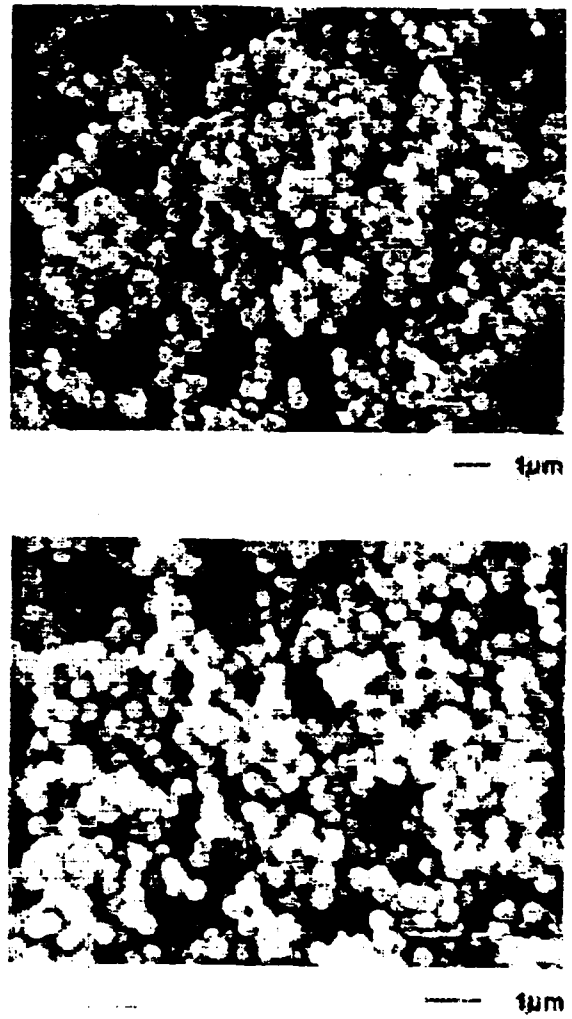


Figure 4. Top. Nickel powder from $Ni(OH)_2$. Bottom. Nickel powder from $NiCl_2$.

in acid or basic solution as suggested in Figure 2. For basic solutions, the rate of formation of methoxido complex formed from the oxonium complex is catalyzed by the presence of free base. In acid solutions, the methoxido complex is destabilized and a higher reduction temperature is required to pass directly from the oxoniun complex to the hydrido complex. These mechanisms are quite speculative at this time. Table I contains the reactant concentrations and reaction times for complete reduction. The time needed for precipitation of the resultant metal powder depends dramatically on the nature of the starting materials chosen. Longer times (24-48 hrs) for the reduction to go to completion are necessary when starting with the commercial cobalt hydroxide than when NaOH is present to catalyze the reduction reaction. This procedure results in cobalt particles within the 1 to 7 micron mean diameter range. By addition of sodium hydroxide to the commercial cobalt hydroxide reaction mixture, a 90 %

savings in time can be gained, with a corresponding decrease in final particle diameter, i.e., the nucleation density is much higher and the reduction reaction proceeds much faster with morphology changing from diffuse to smooth.

When using the cobalt chloride hexahydrate - sodium hydroxide - ethylene glycol solution, a stoichiometrically equivalent amount of sodium hydroxide is necessary to prepare the metal hydroxide intermediate, which precipitates highly dispersed in the heated solvent. From this intermediate, a finer cobalt metal powder is produced (as in photomicrograph bottom of Figure 1). This chemistry yields micron and submicron particles. As the initial concentration of the cobalt chloride hexahydrate is increased, the resultant average particle diameter decreases with an accompanied narrowing of the size distribution. This indicates that an increase of metal salt concentration increases the nucleation rate more than the rate of particle growth, therefore, a large number of smaller particles are formed. It is noteworthy that using an excess of cobalt chloride hexahydrate yields highly aspherical and nodular particles as in Figure 3. The use of cobalt acetate - sodium hydroxide - ethylene glycol also yields aspherical particles with a unique rose petal appearance (bottom photomicrograph, Figure 3).

These particles produced using the polyol reduction method were found not to be pyrophoric upon exposure to air in contrast to some metal powders produced within inert environments of the same micron size range. This observation suggests that the surface of the metal particles may be coated with a metal hydroxide or metal glyoxide. The behavior of cobalt particles in associated nucleation/undercooling work show surprising levels of very high undercoolings. Futhermore, the study of the magnetic properties of these submicron cobalt particles indicates that they are madeup of at least two levels of subunits, the smallest grain sizes being approximately 10 nanometers by X-ray diffraction line broadening, see below. The next level of structucre by SEM analysis appears as 0.01 to 0.05 micron particles which aggregate to form the particles imaged in Figure 3. Again, this finding may be attributable to the maintenance of an unusual surface coating on the finest cobalt particles which precipitate from solution.

The X-ray powder diffraction analysis was conducted on a Siemens D500 system interfaced to a personal computer for data reduction and display. A copper anode x-ray tube (settings @ 30mA and 40kV) was used for the x-ray source. An x-ray beam monochromator was in place during the experimental runs. The powdered metal was loaded into aluminum sample holders and scanned from 25 to 105 degrees (2θ). Both as-prepared and inert-gas heat-treated (1073K/15 min) powder samples were run for copper, nickel and cobalt and nickel cobalt alloys.

X-ray diffraction analysis of chemically quenched cobalt shows a microcrystalline structure for the

powder prepared from the $Co(OH)_2$ precursor (see Figure 5, top). The diffraction peaks have broadened to the characterisitic hill-like structure of amorphous/microcrystalline materials. Upon thermally treating the samples to 1073K/15 min in N_2, the crystallinity of the powder increases, although not to the final equilibrium form (see Figure 5, middle). This heat treatment is hot enough to effect an amorphous or microcrystalline to fully crystalline transition. A commercially prepared cobalt sample (Alpha products, -325 Mesh) XRD powder pattern is shown in Figure 5, bottom, for comparison. For copper and nickel, the x-ray diffraction pattern was always that of the stable FCC structure.

Figure 4 contains SEM results for nickel powders precipitated using similar procedures as for cobalt powders. Specifically, the top photomicrograph shows the morphology for nickel produced from a heated suspension of nickel hydroxide/ethylene glycol. Note that these particles are not as large as their cobalt counterparts, nor is the surface texture as diffuse. Size distributions are unif [1]and submicron for reaction times of the order of 24 hrs (see Table 1). The bottom photomicrograph in Figure 4 depicts uniform nickel powder from a heated solution of nickel chloride hexahydrate/sodium hydroxide/ethylene glycol. Again, these particles are approximately 0.5 microns for d. Surface morphology is similar for both preparative chemistries. Aspherical nickel powder has been produced by reducing nickel acetate tetrahydrate.

Five cobalt-nickel alloys were prepared with compositions 80/20, 60/40, 50/50, 40/60 and 20/80 cobalt/nickel, respectively. These powders were prepared from the metal chlorides precipitated as hydroxides by sodium hydroxide and reduced in ethylene glycol. The reductive potentials of both cobalt and nickel salts in non-aqueous polyol solutions were approximately equal yielding metal alloy powder precipitates in the same mole percent ratio as the initial reactants. The reactions were complete in three hours and the resulting particles were all spherical, uniform and with values for d of between 0.5 and 1.0 microns. The melting point of each of the alloys was determined by DTA and agreed closely with the values given for the liquidus of the cobalt-nickel system[8]. The melting points were 1742K, 1728K, 1727, 1716 and 1713K for the 80/20, 60/40, 50/50,40/60 and 20/80 alloys respectively.

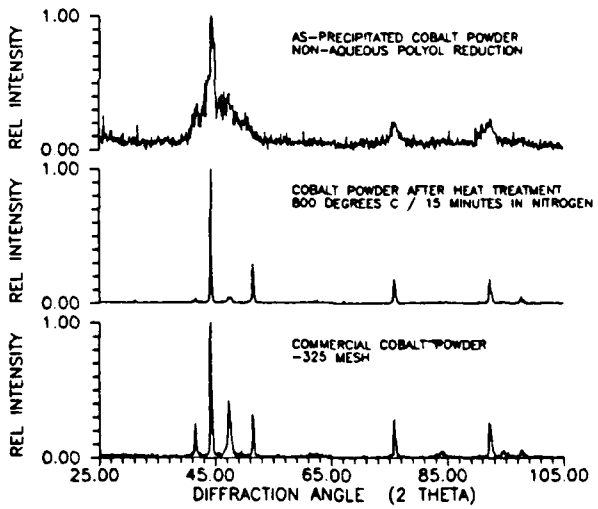
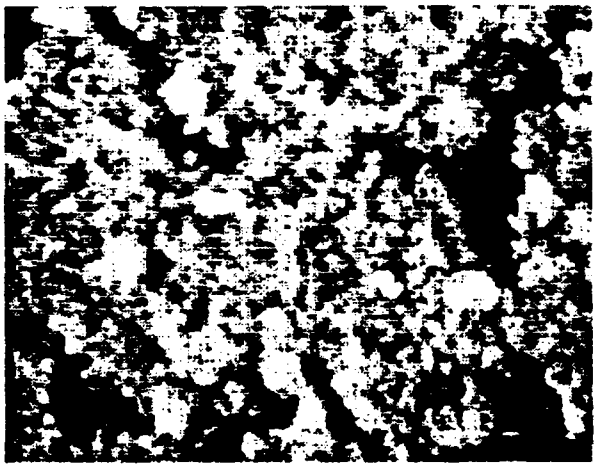


Figure 5. X-ray diffraction of as reduced microcrystalline Cobalt powder, top; heat treated and crystallized Cobalt powder, middle and reference powder, bottom.

B. OTHER METAL POWDERS

Palladium, copper, silver, lead and bismuth metals have all been reduced from nonaqueous solution in a monodispersed state. These metals are more noble that cobalt or nickel and are easily reduced in the polyol environment. In fact, the ease of reduction of these metals lead to a modification of the polyol reduction process which utilizes dimethylformamide (DMFA), dimethyacetamide (DMAA) or dimethylsulfoxide (DMSO) as solvent and reductant. Reflux of the metal nitrate in these solvents at 423K, with or without surface active additives such as polyvinylpyrrolidone (PVP), ethylene glycol (EG), or ethylenediamine tetraacetate (EDTA), will produce narrow size distribution uniform metal powders.



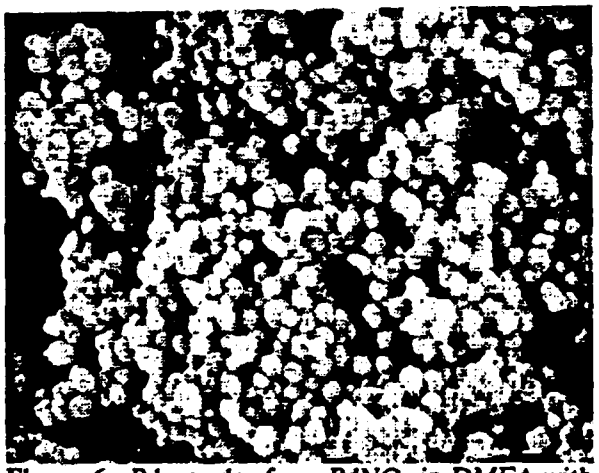


Figure 6. Pd powder from $PdNO_3$ in DMFA with ethylene glycol and polyvinylpyrrolidone, top. Pd powder from $PdNO_3$ in DMFA. Long bar, 1 μm.

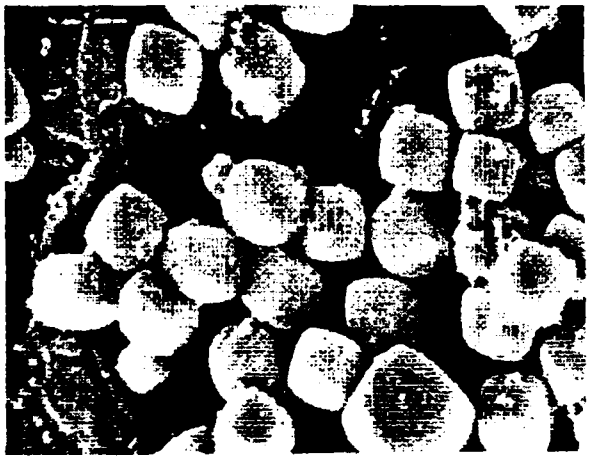


Figure 7. Cu powder reduced from DMFA with EG and PVP present, top. Cu powder reduced from DMFA with no surface additive, bottom.

Figure 6 presents photomicrographs of palladium powder generated by reduction in DMFA with and without surface active additives. The presence of the surface active compounds significantly decreases the mean particle size. It was not possible to generate uniform size distribution powders of palladium with mean particle sizes greater than 1 micron diameter.

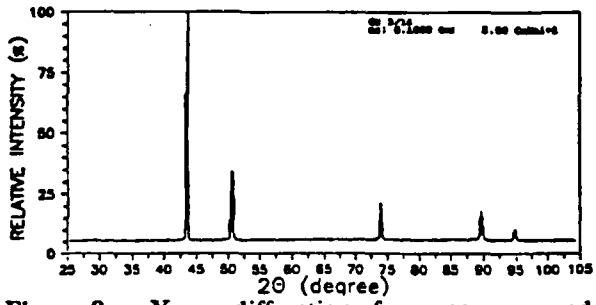
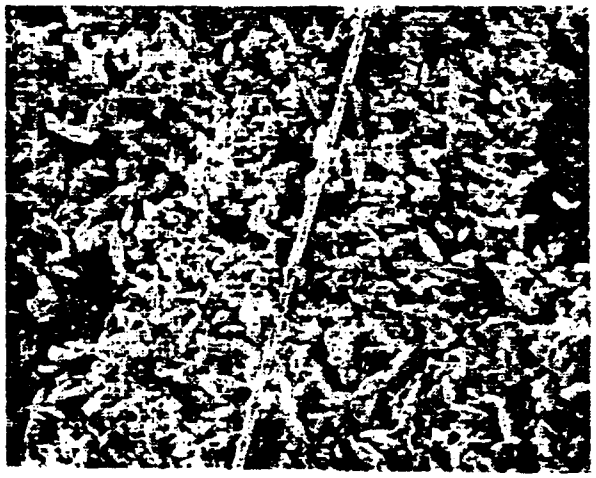


Figure 8. X-ray diffraction from as prepared copper powder.



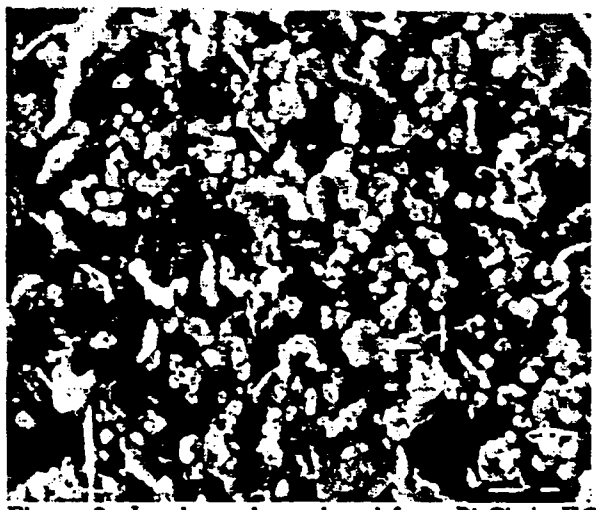


Figure 9. Lead powder reduced from $PbCl_2$ in EG (top) and from $PbC_2H_3O_2$ in EG (bottom). Top particles 5 micron footballs in length, bottom particles, platelets with 0.1 micron thickness.

Figure 7 presents photomicrographs of copper powder reduced from dimethylformamide with and without surface active additives. The ease with which copper can be reduced does not limit the growth of the copper particles with clearly cubic forms dominant in the bottom photomicrograph and rounded cubic forms evident in the top photomicrograph. Note the distinctive sharp surface characteristics (edges and corners) as well as growth twins and dislocation controlled overgrowth evident in the bottom photomicrograph. These features of the nonaqueous reduction process are smoothed over in the presence of surface active additives.

Figure 9 presents photomicrographs of lead powders reduced from ethylene glycol by thermal decomposition of the ethylene glycol. Here, the upper photomicrograph is of football shaped lead particles reduced from lead chloride and the bottom micrograph is of platelet lead particles reduced from

lead acetate.

II. UNDERCOOLING AND NUCLEATION OF LIQUID METALS

The kinetics of nucleation of crystals from undercooled melts can be determined by the use of the droplet emulsion technique originally advanced by Vonnegut and perfected by Turnbull for liquid in liquid suspensions. The droplet emulsion technique consisted of suspending metal particles or emulsifying metal droplets in a stable carrier fluid such that each droplet is held independent of all the other droplets of metal by a surface coating capable of preventing reversion of the emulsion to bulk liquid phases. If the surface coating did not act as a nucleator of the solid metal, the entire emulsion could be undercooled substantially below the melting point. Rasmussen advanced the techniques required to form droplets with less active nucleation sites for metal nucleation and crystallization and he and Perepezko and coworkers then fruitfully applied this methodology. Since the droplet emulsion technique suffered from the lack of carrier fluids which did not interact with the metal at high temperatures, attempts at using the method with fused salts as carrier fluids have had only varying success. The recent modification of the droplet emulsion technique entitled solid in solid suspensions has overcome the problem of a lack of carrier fluids for high temperature dispersions. Instead of using a carrier fluid, a dispersion of the metal powder is made in a second much higher volume fraction submicron ceramic powder. The use of levigated 0.05 micron diameter alumina powder has become standard. This dispersion is prepared in an organic solvent which contains any desired surfactants for treating the metal particles. The complete suspension is filtered and dried such that the metal powder is uniformally dispersed in the alumina matrix. On heating, the alumina compacts and encapsulates the individual metal particles as in the droplet emulsion technique. The metal can then be melted and undercooled as distinct and separate metal droplets. This sample preparation technique when combined with the uniform as precipitated metal powders discussed above permits undercoolings to nucleation as large as have been observed by any other bulk technique. Only for angstrom diameter electron microscope condensate clusters (which may not exhibit bulk liquid behavior are larger undercooling reported).

Because the powder metal dispersed in alumina provides a droplet distribution capable of individual droplet crystallization without nucleation and crystallization of any other droplet, these solid-in-solid dispersions can be used for the study of the kinetics of nucleation of undercooled liquid metal. Furthermore, because the undercoolings observed with metals suspended in the alumina are as large as undercoolings observed for these metals in any other suspension method, the possibility of observing homogeneous nucleation exists. The nucleation kinetics were determined for selected metals by

continuous cooling differential scanning calorimetry.

Differential thermal analysis was performed on a Perkin-Elmer DTA 1700 Thermal Analyzer controlled through a system 7/4 Controller and coupled to a Perkin Elmer Thermal Analysis Data Station (TADS). Powdered metal was placed in a ceramic sample cup and heated, under a constant purge of dry argon gas at 40 cc/min, from 373K to 1763K at a rate of 25K/min. Both as-prepared and inert-gas heat-treated (1273K/15 min) powder samples were run. Melting points were obtained with the DTA system. For these samples, metal droplet coagulation occurred on melting and the cycled melting points for bulk samples were determined. In the nucleation study, the metal powders were dispersed in an appropriate ceramic media (e.g., Levigated alumina powder of approximately 0.05 micron diameter) to form a solid-in-solid suspension. The metal powder volume fraction of about 5 to 10 vol per cent. For these samples nucleation rate versus undercooling by constant cooling differential scanning

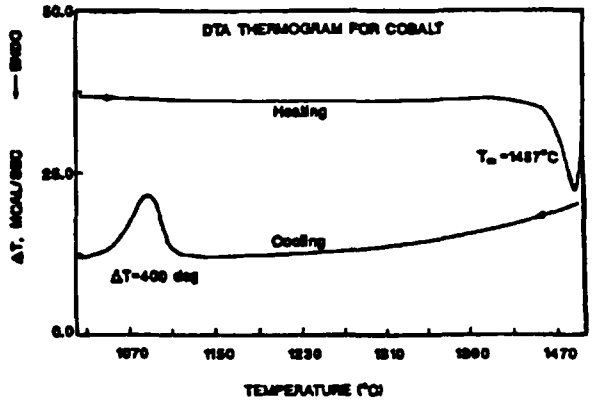


Figure 10. Heating and cooling thermogram for cobalt powder dispersed in alumina.

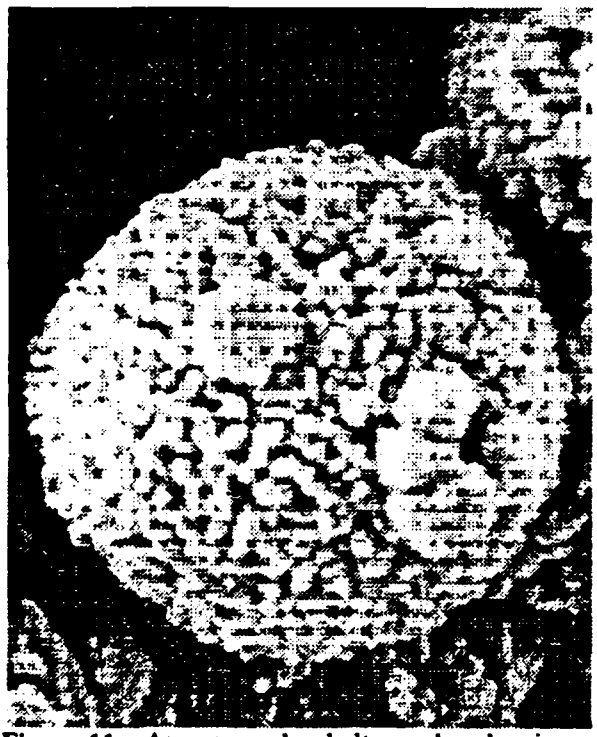


Figure 11. As prepared cobalt powder showing a high state of subdivision. X-ray pattern corresponds to top curve in figure 5.

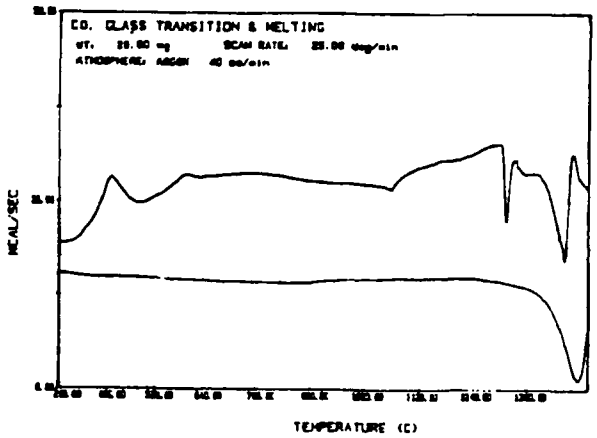


Figure 12. Heating thermograms for microcrystalline cobalt powder. Upper curves as prepared. Lower curve for recycled powder.

By following the same procedure as used in the cobalt studies, DTA thermograms were determined for the nickel powders to determine the melting points and heats of fusion. Both melting temperature T_m = 1758 ± 5 K and heat of fusion ΔH = 61.3 cal/gram were in agreement to literature values [5]. The kinetics of nucleation can be determined from the combined knowledged of the sample mass, the size distribution and the shape of the constant cooling rate thermogram. The instantaneous rate of nucleation is determined as presented in Figure 14. The droplet size distribution comes into play as the existing mean unfrozen droplet size is required to transform the nucleation rate per droplet into a nucleation rate per unit volume at temperature T. The temperature dependence of the nucleation rate is then readily determined from the composite set of rates calculated for each instant of time during the continuous cooling process. It is not possible to determine whether the nucleation process is dependent on the area of the surface of the droplets or dependent on the volume of the droplets, i.e. whether the nucleation process is heterogeneous or homogeneous from the continuous cooling experimental measurements. This inability is due to the possible nonuniformity of temperature within the experimental sample at any particular average cell temperature during constant cooling and/or any shift in the mean of the size distribution with total fraction transformed. Without knowing the mechanism *a priori* the form of the change in the mean size with fraction transformed cannot be evaluated and without knowing the change in the size distribution with total fraction transformed, the mechanism cannot be determined. Therefore, the experimental results have been plotted as if a homogeneous nucleation process has been observed and the temperature dependence of the nucleation process has then been used to determine the parameters of the theory.

Figure 15 presents the experimental data for the major peak observed at an undercooling of 400 degrees for 0.5 micron Cobalt powder suspended in alumina. Because there is a smaller exothermic peak at about 490 degrees undercooling, this peak represents a heterogeneous nucleation process. The temperature dependence, however, can be determined on the basis of the mean droplet volume rather than the mean droplet surface area since there is a simple geometric relationship between the two. It is not known whether the heterogeneous catalyst is located at the surface of the droplet or is suspended randomly in the droplet volume. If the later is the case then the heterogeneous nucleation rate will be proportional to the droplet volume as given in the following formulae.

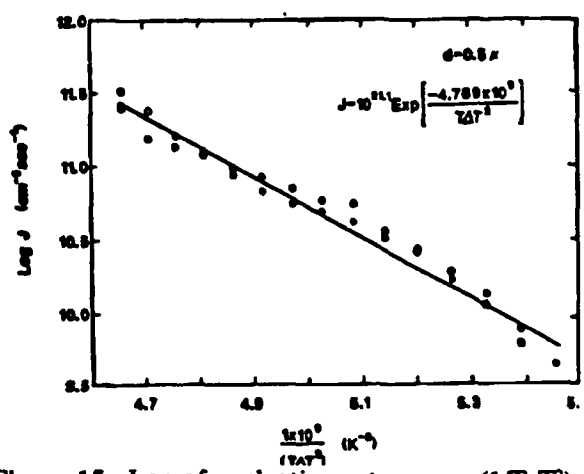


Figure 15. Log of nucleation rate versus $(1/T\Delta T^2)$.

$J_{het} = A \exp\{ - b/(T\Delta T^2)\}$

where $A = 10^{21.1}$ and $b = 4.769 \times 10^9$. There is not much point speculating on the meaning of b in terms of the surface free energy per unit area of solid liquid interface since the contact angle is not known.

Analysis of the thermogram exotherm at 490 degrees of undercooling yields results which are much more in line with the expectation of homogeneous nucleation with $A = 10^{26}$ and b = . The sets of data presented in Figure 16 are for cobalt samples with the following means droplet sizes, 0.66+0.05 , 1.13+0.23, 1.2+0.23, 2.9+0.3 and 3.43+0.37 microns as determined from post nucleation distribution of the droplet sizes within the sample. While this result is consistent with homogeneous nucleation, because only a small percentage of the sample reached this high undercooling, it is not possible to conclude that indeed homogeneous nucleation has been observed. In fact, there is reason to believe that the classical nucleation theory is incorrect and that the temperature dependence to which these data have been plotted are incorrect.

III. ASPECTS OF RATE MEASUREMENTS AND NUCLEATION THEORY

The validity of the assumptions which permit calculation of a nucleation rate from measurement of bulk thermal effects is being tested in a program which is part of this research. The use of differential thermal analysis and differential scanning calorimetry to test nucleation theory is currently only parti lly complete and will be ongoing after the termination of this program. The issue is whether or not nucleation within one droplet can be considered to be independent of the presence a large number of surrounding droplets which are also undergoing nucleation and crystallization. If the phase change in any one drop disturbs the assumption of local isothermality of the sample, then the stochastic character of the nucleation process is affected because larger droplets will influence their neighbors is a more significant manner than will small droplets. Both the temperature rise and the time away from isothermality will be greater around large crystallizing droplets than around small droplets and small droplets will be heated to higher

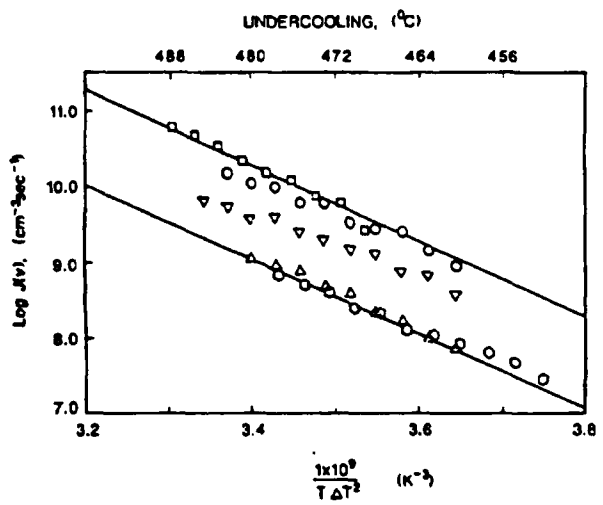


Figure 16. Log J versus $(1/(T\Delta T^2))$ for the lowest temperature, highest undercooling peak for five separate cobalt powders.

temperatures than will neighboring larger droplets. In addition to this thermal response, the impact of any shock or pressure wave created by the phase transition will impact other droplets in the distribution in a manner dependent on the radius of the droplet rather than according a surface area or volumetric effect on nucleation. Remember that Turnbull used observation the "blick", visual, as well as the "click", sound effect, to note when individual droplets crystallized on a hot stage microscope. The results to date indicate that a general model incorporating the heat transfer effects can be formulated which basically parallels the assumptions of isothermality in terms of nucleation rate versus temperature and the ability to separation a surface dependent from volume dependent nucleation process. However, if the pressure waves can affect droplets across the sample, then the nucleation rate will be distorted by a process which scales with the collision cross section with the wave and thus with the diameter of the droplet. Such a process has not yet been demonstrated for metal powders but may have been observed in earlier studies on undercooled water by the author. The result of this part of the project will be completed in the near future.

In addition to modelling the determination of nucleation rates using differential thermal analysis and differential scanning calorimetry, the whole concept of homogeneous nucleation in the classical framework has been investigated[9,10]. The capillarity approximation of classical theory (that both phases are bulk phase separated by an interphase which has the properties of a planar interface between bulk phase) was originally made by J. W. Gibbs because this fixed the chemical potential within the nucleus and the magnitude of the surface free energy per unit area of cluster surface. Without this or some similar approximation, it would have been impossible to calculate the work of formation of a nucleus because equations of state and models for the surface tension versus the difference in density across the interface had not yet been developed. Gibbs demonstrated that for systems not far removed from equilibrium his approximation was a good first attempt at the determination of the free energy of formation of a nucleus. However, at high supersaturation or undercooling typical of homogeneous nucleation phenomena, the number of atoms or molecules in a critical nucleus is so small that the validity of Gibbsian approximation is in doubt.

A new capillarity approximation has been formulated and applied to the classical problem of condensation from the vapor, the corollary nucleation of bubbles from a superheated liquid and for liquid-liquid phase separation. The application to crystal nucleation from undercooled liquids is currently being developed. This new capillarity approximation is an equation of state approximation and the properties of a small droplet or cluster are no longer tied to those of "equilibrium bulk phase behavior"; instead, the interior of the cluster is treated as a fluid which obeys the same interaction potentials and has the same equation of state as a bulk fluid with the same density modified to include the increased Helmholtz potential due to the interface. The interface is given an energy equivalent to

that associated with the van der Waal's treatment which is consistent with a surface energy which is a function of the difference in density across the interface. The combination of an equation expressing the energy of the interior of a cluster as a function of it's density and the interfacial free energy as a function of the density difference across the interface permits the calculation of the free energy of formation of any cluster size at any density for that cluster. Thus the new capillarity approximation removes the "incompressible" character of classical nucleus. While is not so important in crystal nucleation from the liquid, it is certainly an improvement for the nucleation of gas bubbles from condensed phases. Even in condensed systems, the removal of the incompressibility of the nucleus gives an added degree of freedom to the cluster. That is, bulk free energy can be exchanged for surface free energy through expansion of the cluster with decrease in internal pressure but at the expense of an increase in surface area with a decrease in the surface tension because the density difference across the interface decreases. Similar arguments can be made for degrees of order across the liquid - crystal nucleus interface.

The result of this modelling work is a modification of the Laplace relation when systems are supersaturated or undercooled. Also the thermodynamic criterion which apply to bulk phase equilibrium now apply to the nucleus liquid unstable equilibrium. The effect on the models of nucleation rates is to increase the steepness of the nucleation rate on supersaturation or undercooling. For the liquid solid nucleation process the log of the nucleation rate becomes proportional to the reciprocal of the third power of the undercooling. This change in the model of nucleation, if proven correct, will negate all former calculation of the surface tension between solid and liquid metals from the application of the classical theory of nucleation. At this stage, these calculation are certainly cast in dubious light.

IV. SUMMARY

A technique for the production of uniform submicron to micron sized metal powders has been developed and applied to cobalt, nickel, silver, copper, lead and bismuth. The metal reduction process occurs because polar organic liquids act as reducing agents at high temperatures. The metal powders possess narrow size distributions with d ranging from 0.1 to 7 microns. Standard deviations of particle populations are on the order of 0.1d. Particle surface morphology can be controlled by choice of metal-containing reactant species. Spherical or aspherical (nodular or rose-petal shaped) appearances have been reproducibly produced. DTA results from melting point and heat of fusion measurements show good agreement with known purity metal standards and suggest low impurity levels. DTA analysis yields the presence of an irreversible exothermic transition within the temperature range of 676-773K in cobalt metal powders prepared from a $Co(OH)_2$ precursor. XRD results indicate amorphous/microcrystalline structure for the as prepared cobalt from the same hydroxide precursor.

Thermal treatment of the amorphous / microcrystalline sample yields a crystalline yet still non-equilibrium form as evident in XRD spectra. The solid-in-solid suspension technique has permitted to study of the undercooling of these uniform metal powders with the result that significantly large undercoolings have been observed. Because of the inability to carry out isothermal differential scanning calorimetric measurements at high temperatures, the nucleation rates have been determined from constant cooling differential scanning calorimetry. The validity of the measurement is currently being evaluated because of assumptions which have been made in the data reduction procedure may be incorrect. Finally, the whole classical theory of homogeneous nucleation has been challenged on the grounds that the capillarity approximation made by Gibbs over 100 years ago can now be replaced with a better equation of state approximation. The result is a modification in the energetics of nucleus formation and a change in the influence of supersaturation or undercooling on the rate of new phase nucleation.

V. PUBLICATIONS

Don H. Rasmussen and Kazi Javed, "Undercooling and Nucleation in Iron-Nickel Alloys", in Undercooled Alloy Phases, Eds. E. W. Collings and C. C. Koch,pp. 79-94, The Metallurgical Society, Inc. Warrendale, PA (1987).

Dennis Kiriakidis, "Preparation of Monodispersed Cobalt, Nickel, and Cobalt-Nickel Alloy Powders by Reduction in Polyols", M. S. Thesis, Clarkson University, Potsdam, NY 1987.

Don H. Rasmussen, Etop Esen and Mary Appleby, "The Critical Complex in Nucleation Theory is not the Nucleus. Part 1. A Laplace Relation for Supersaturated Systems," submitted for publication in the Journal of Colloid and Interface Science.

Don H. Rasmussen, Etop Esen and Mary Appleby, "The Critical Complex in Nucleation Theory is not the Nucleus. Part 2. Condensation," submitted for publication in the Journal of Colloid and Interface Science.

Kazi Javed, "Nucleation Kinetics of Monodispersed Undercooled Liquid Metal Droplets," Ph.D. Dissertation submitted and defended October, 1987, in partial fulfillment of the Ph.D. degree at Clarkson University.

Dontula Narasimharao, "Excimer Laser and Thermally Induced Deposition of Metal Powders and

Nucleation Kinetics of Lead," M.S. Thesis, Clarkson University, Potsdam N.Y. 1989.

Robert L. Bush, Dionissios G. Kiriakidis and Don H. Rasmussen, "Chemically Quenched Powders of Cobalt, Nickel and Cobalt/Nickel Alloys: Preparation and Undercooling," J. Materials Research (submitted for publication.)

Sigurds Arajs, Louis C. Nanna, Don H. Rasmussen and Robert L. Bush, "Hysteretic Behavior of Cobalt Powders," to appear in the J. Applied Physics, May 1990.

Dontula N. Rao, S. V. Babu, and Don H. Rasmussen, "Laser Induced Deposition of Copper and Lead Powders," A.I.Ch.E. Journal, (submitted for publication).

VI. REFERENCES

1. Figlarz, M., Fievet, F., and Lagier, J. P., French Patent No. 2537898 (1982).

2. Kiriakidis, D.G., Masters Thesis, *Preparation of Monodisperse Cobalt, Nickel and Cobalt-Nickel Alloy Powders by Reduction in Polyols*, Clarkson Univ., May, 1987.

3. Neville, H.A., J. Phys. Chem., 30, 1181-1184 (1926).

4. Vaidya,B.K., Nature, 123, 414 (1929); *Glycerol*, C.S.Miner and N.N.Dalton, editors, American Chemical Society Monograph Series No.117, Reinhold Publishing Corp. (1953).

5. Robert L. Bush, Dionissios G. Kiriakidis and Don H. Rasmussen, "Chemically Quenched Powders of Cobalt, Nickel and Cobalt/Nickel Alloys: Preparation and Undercooling," J. Materials Research (submitted for publication.)

6. Dontula N. Rao, S. V. Babu, and Don H. Rasmussen, "Laser Induced Deposition of Copper and Lead Powders," A.I.Ch.E. Journal, (submitted for publication).

7. Sigurds Arajs, Louis C. Nanna, Don H. Rasmussen and Robert L. Bush, "Hysteretic Behavior of Cobalt Powders," to appear in the J. Applied Physics, May 1990.

8. *Metals Handbook, 8th Ed., Metallography, Structures and Phase Diagrams*, American Society for Metals, vol.8, p.288

9. D. Rasmussen, E. Esen and M. R. Appleby, manuscript entitled "The Critical Complex in Nucleation is not the Nucleus. Part 1. A Laplace Relation for Supersaturated Systems," submitted to the J. C. I. S.

10. D. Rasmussen, E. Esen and M. R. Appleby, manuscript entitled "The Critical Complex in Nucleation is not the Nucleus. Part 2. Condensation," submitted to the J. C. I. S.